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## (54) METHOD OF CHEMICAL DECONTAMINATION OF METAL STRUCTURAL MATERIAL FOR FACILITY RELATED TO REPROCESSING

## (57)Abstract:

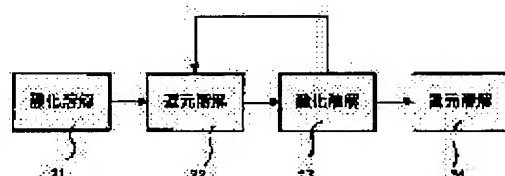
PROBLEM TO BE SOLVED: To enable a method for high-performance decontamination that generates less secondary wastes to be realized by allowing an oxidizer to act on a metal structural material for reprocessing facilities or related facilities, then permitting a reductant to act on it and repeating such processes once at least.

SOLUTION: An oxidation and reduction treatment is conducted in the order of an oxidation dissolution process 21, a reduction dissolution process 22, an

oxidation dissolution process 23 and a reduction dissolution process 24, and further, the oxidation and reduction treatment is repeated alternately if it is

necessary. An ozone water solution or a solution whose oxidation and reduction potential is equal to that of the

ozone water solution or is about 0.8 V or higher is used as an oxidizer. The ozone water solution is prepared by bringing an ozone gas into contact with an acid solution whose pH is conditioned to 5 or lower, and the temperature of the ozone water solution is limited to the range between about 50 and 100°C inclusive. Dicarboxylic acid solutions are used as a reductant. The most appropriate one of them is an oxalic acid water solution, whose concentration is set at about 1,000 to 5,000 ppm and whose temperature is in the range between about 50 to 100°C. The removal ratio of an oxide layer on the surface of a base



material can be heightened by repeating oxidative and reductive decontaminations with such chemicals.

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 DETAILED DESCRIPTION
 

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## [Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] This invention relates to the chemistry decontamination method for dissolving chemically and removing the oxide film containing the radioactive substance adhering to the front face and inner surface of such metal structure material, if the radioactive contamination adhering to a front face and inner surfaces, such as piping of the metal structure material of a reprocessing facility and its related facility, a device, and a structural part, is described in more detail about the chemistry decontamination method for removing chemically.

[0002]

[Description of the Prior Art] Metal structure material, such as piping of a rework related facility, a device, and a structural part, contacts the solid-state or fluid containing the radioactive substance, such as alpha nuclear species, such as uranium and plutonium, and FP (nuclear reaction product). Radionuclide is adhered and accumulated in the contact surface of such the metal structure material and the radioactive substance with operation of rework equipment.

[0003] Therefore, the dose of radioactivity of the authorized personnel at the time of facility modification or an overhaul etc. increases at the time of maintenance inspection of piping, a device, etc. Moreover, in case such metal structure material is discarded, it will be necessary to perform management special as trash polluted with alpha nuclear species.

[0004] in order to decontaminate such radioactive contamination, water, an acid, alkali, an oxidizer, a reducing agent, a chelating agent, etc. are variously independent in various drugs to the chemistry decontamination method of dissolving chemically and removing the radioactive substance, the place to current -- or it combines and uses.

[0005]

[Problem(s) to be Solved by the Invention] In the conventional chemistry decontamination method, it is the object which heightens the decontamination effect, and since [ which uses various drugs variously ] it mentioned above, secondary trash, such as decontamination waste fluid, is generated so much after decontamination. Great costs and time amount were spent on processing of these secondary trash and disposal, and the case which is not received in a disposal field is also generated.

[0006] Therefore, recently, it has become difficult to apply the chemistry decontamination method to the system only on the basis of the high level of the decontamination engine performance, and to optimize as the whole decontamination system is demanded in consideration of a gestalt, an amount, etc. of costs, time amount, and the generated secondary trash.

[0007] Especially, in the decontamination at the time of periodical device exchange, decontamination in a decontamination pin center, large, etc., it is the range of the decontamination engine performance made into the object, and it is necessary to reduce the yield of secondary trash, and the effect on environment as much as possible.

[0008] This invention was made in order to solve the above-mentioned technical problem, and it aims at offering the chemistry decontamination method of the metal structure material of a reprocessing facility

or its related facility with little generating of secondary trash with the high and decontamination engine performance.

[0009]

[Means for Solving the Problem] As indicated to claim 1, a chemistry decontamination method of this invention has an oxidation process which makes an oxidizer act on metal structure material of a reprocessing facility or its related facility, and a reduction process which makes a reducing agent act on said metal structure material, and is characterized by repeating said oxidation process and said reduction process once or more.

[0010] According to such a configuration, decontamination engine performance which raised an elimination factor of contamination, such as an oxide film of a metal structure material front face, and was excellent in repeating oxidation / reduction decontamination processing is obtained. An oxidation process and a reduction process can also perform which previously.

[0011] As indicated to claim 2, it is desirable that it is the ozone aqueous solution with which said oxidizer contacted ozone gas in a with a pH of five or less acid aqueous solution, and was prepared, and said reducing agent is a dicarboxylic acid aqueous solution.

[0012] Since it an ozone aqueous solution and a dicarboxylic acid aqueous solution not only show oxidizing power which was excellent, respectively, and reducing power, but can disassemble decontamination waste fluid after using it for a decontamination process into oxygen, a carbon dioxide, water, etc., they can decrease in number a secondary trash yield.

[0013] Moreover, as indicated to claim 4, it is desirable that said acid aqueous solution is a nitric-acid aqueous solution. It is because high oxidizing power of an ozone aqueous solution can be used efficiently.

[0014] As indicated to claim 3, a solution which has a oxidation-reduction potential equivalent to an ozone aqueous solution which ozone gas was contacted in a with a pH of five or less acid aqueous solution, and was prepared as said oxidizer, or a oxidation-reduction potential beyond 0.8V may be used.

[0015] Such a solution has engine performance in which a oxidation-reduction potential was highly excellent as an oxidizer. Moreover, decontamination waste fluid reacts with drugs, such as oxalic acid, and serves as water and a carbon dioxide, and since trash serves as only some metal ions, it can decrease in number a secondary trash yield.

[0016] As indicated to claim 5, as for said dicarboxylic acid aqueous solution, it is desirable that it is an oxalic acid aqueous solution with a concentration of 1000 ppm - 50000 ppm. It is because the reduction decontamination effect can disassemble decontamination waste fluid into water and a carbon dioxide highly.

[0017] In said oxidation process, as indicated to claim 6, it is desirable to hold said oxidizer at 50 degrees C - 100 degrees C. Moreover, in said reduction process, as indicated to claim 7, it is desirable to hold said reducing agent at 50 degrees C - 100 degrees C. By performing a decontamination process at low temperature comparatively, energy expenditure required for temperature maintenance can be reduced.

[0018] It is especially performing an oxidation process and a reduction process on the same temperature conditions in system decontamination etc., and since [ without temperature up of decontamination liquid between processes and a temperature fall ] it can process continuously, working hours can be shortened.

[0019] As indicated to claim 8, it may let said oxidizer and said reducing agent flow to a reprocessing facility system. A system piping device inner surface can be decontaminated efficiently to decontaminate the whole system or a part, without using a special decontamination tub.

[0020] it indicated to claim 9 -- as -- said oxidation process -- setting -- said oxidizer -- an oxidation tub -- holding -- this oxidizer -- said metal structure material -- predetermined time amount immersion -- carrying out -- said reduction process -- setting -- said reducing agent -- a reduction tub -- holding -- this reducing agent -- said metal structure material -- predetermined time amount immersion -- it may be made to carry out.

[0021] an oxidizer and each reducing agent -- by using a decontamination tub of dedication, the

multiple-times activity of the decontamination reagent is carried out, and generating of secondary trash can be reduced.

[0022] In such a case, ultrasonic cleaning of said metal structure material may be performed in either [ at least ] said oxidation tub or said reduction tub. By preventing a residual or reattachment of contamination chemically dissolved by oxidation / reduction decontamination, improvement in clearance engine performance and compaction of decontamination time amount can be aimed at.

[0023] As indicated to claim 11, in said oxidation process, a oxidation-reduction potential of said oxidizer may be measured and oxidizing power of said oxidizer may be controlled based on the measured value. By supervising and adjusting oxidation engine performance on real time, efficient decontamination processing is possible.

[0024]

[Embodiment of the Invention] It is made to dissolve in the decontamination reagent side which is a drug solution chemically, and chemistry decontamination removes the radioactive substance adhering to a metal base material. Therefore, in the chemistry decontaminating method of the conventional rework related facility, it was common to have selected a decontamination reagent from a viewpoint which carries out dissolution clearance of the radioactive substance, such as uranium, plutonium, and FP nuclear species, from metal structure material.

[0025] However, in selection of the chemistry decontaminating method, it is necessary to take into consideration what kind of the radioactive substance has adhered to the metal base material front face with what kind of contamination gestalt. That is, whether it is incorporated that the radioactive substance has adhered independently or in other matter, whether a contamination gestalt has change in the depth direction or there being any corrosion of a base material, and information are important.

[0026] However, there was no detailed report about the contamination gestalt of the metal structure material of a rework related facility until now. Then, when investigated for stainless steel structure material about the contamination gestalt in alpha nuclear species of the metal refuse used in the reprocessing facility, as shown in a table 1, it was able to divide into three patterns of the contamination patterns A, B, and C. The typical cross section near [ corresponding to each contamination pattern ] a metal structure material front face is shown in drawing 1 (a), (b), and (c).

[0027]

[A table 1]

α汚染廃棄物性状調査

	汚染パターンA	汚染パターンB	汚染パターンC
使用環境	硝酸系 100℃ 溶解槽	硝酸系 100℃ 蒸发器	有機系 室温 ミキサセトラ
汚染核種	α核種+FP	α核種	α核種
母材腐食	母材腐食有り (粒界腐食)	母材腐食有り (粒界腐食)	母材腐食無し
汚染形態	酸化物層 付着物 粒子付着物	酸化物層 — —	— — 粒子付着物

As shown in the contamination pattern C and drawing 1 (c) of a table 1, in the structure material used in the room temperature system of an organic system like a mixer settler, there is almost no corrosion of the stainless steel base material 1, and it turned out that the radioactive substance 3 which is a contamination has only adhered to the front face of the stainless steel base material 1. What is necessary is to dissolve the radioactive substance 3 and just to remove like a conventional method, in order to decontaminate such contamination.

[0028] As shown in the contamination patterns A and B of a table 1 and drawing 1 (a), and (b), in the structure material used in the elevated-temperature system of a nitric-acid system like a dissolver or an evaporator, it was checked that the front face of the stainless steel base material 1 has received

intergranular corrosion (base material corrosion 4) considerably. Furthermore, the thin oxide film 2 with high Cr content was formed in the front face of this stainless steel base material 1 and intergranular corrosion (base material corrosion 4). It turned out that the radioactive substance was incorporated by this oxide film 2, or the radioactive substance 3 has adhered to it on this oxide film 2. The oxide film 2 formed in the front face of the carrier beam stainless steel base material 1 in intergranular corrosion is expanded, taken out and shown in the right-hand side of drawing 1 (b).

[0029] It is difficult to acquire the decontamination effect beyond 90% clearance (DF10) or 95% clearance (DF20) by the method of dissolving and removing the radioactive substance 3 with a contamination gestalt like such contamination patterns A and B. In order to acquire the high decontamination effect beyond 99% clearance (DF100) and 99.9% clearance (DF1000), it becomes important to dissolve and remove the thin oxide film 2 formed in the front face of a base material 1 and intergranular corrosion (base material corrosion 4) rather than dissolving radioactive substance 3 the very thing.

[0030] Then, we decided to offer the decontaminating method which attains the high decontamination engine performance and minimum-izes the yield of secondary trash by dissolving selectively efficiently the thin oxide film 2 which exists between a contamination and a base material based on the above-mentioned contamination gestalt results of an investigation.

[0031] Hereafter, the example of this invention is explained with reference to a drawing. The explanation which attaches the same sign and overlaps is omitted about the same component. In addition, this invention is not limited to the following example, within limits which do not change the summary, deforms suitably and can be carried out.

[0032] (Example 1) Drawing 2 is flow drawing of the decontamination method concerning this example. Oxidation / reduction processing is performed in order of the oxidizing melting process 21, the reduction dissolution process 22, the oxidizing melting process 23, and the reduction dissolution process 24. If required, return and oxidation / reduction processing will be repeated at the reduction dissolution process 22 from the oxidizing melting process 23.

[0033] Although the radioactive substance, such as uranium, plutonium, and FP nuclear species, exists as an oxide of  $\text{UO}_2$ ,  $\text{PO}_2$ , and  $\text{RuO}_4$  grade, respectively, in an operation of an oxidizer, it becomes ion, such as  $\text{UO}_2^{2-}$ ,  $\text{PO}_2^{2-}$ , and  $\text{RuO}_4^{2-}$ , and it dissolves.

[0034] The thin oxide film which exists between the radioactive substance and metal base materials, such as stainless steel, is the iron chromic-acid ghost of  $\text{FeCr}_2\text{O}_4$  with the high content of chromium. The iron oxide has taken the oxide gestalt of  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  grade, in an operation of a reducing agent, becomes  $\text{Fe}^{2+}$  and dissolves. The chromic-acid ghost has taken the oxide gestalt of  $\text{Cr}_2\text{O}_3$  grade, and chromium trivalent in an operation of an oxidizer turns into chromium of 6 \*\*, such as  $\text{CrO}_4^{2-}$  and  $\text{Cr}_2\text{O}_7^{2-}$ , and it dissolves.

[0035] Therefore, in order to dissolve the oxide  $\text{FeCr}_2\text{O}_4$  of an iron chromium mixed form, in the reduction dissolution independent which used the reducing agent, dissolution of chromium cannot be performed and the high decontamination engine performance is not obtained. moreover, the oxidizing melting which used the oxidizer -- if independent, chromium oxidizes to 6 \*\* and it becomes easy to dissolve it, but since oxidizing melting is not carried out, iron is not dissolved as the oxide  $\text{FeCr}_2\text{O}_4$  whole which is the mixture of chromium and iron.

[0036] Then, if a reducing agent is made to contact like this example after making an oxidizer contact, it oxidizes, reduction dissolution of the chromium which becomes easy to dissolve is carried out with iron, and the iron chromic-acid ghost  $\text{FeCr}_2\text{O}_4$  can be removed. Therefore, by using the oxidation / reduction decontaminating method which repeats an oxidation process and a reduction process, the oxide film which exists between the radioactive substance and the radioactive substance, and a metal base material is dissolved, and the outstanding decontamination engine performance can be attained.

[0037] It is desirable to usually repeat it about twice, although it is good in a line by a unit of 1 time and such an oxidation / reduction process is depended also on the thickness of an oxide skin and a gestalt. Moreover, although it is usually desirable to perform an oxidation process previously, when the ferric acid ghost with easy reduction dissolution has covered the front face thickly for example, a reduction

process may be performed first.

[0038] As an oxidizer used in the oxidizing melting processes 21 and 23, an ozone aqueous solution or a oxidation-reduction potential is preferably used for a certain solution etc. an ozone aqueous solution, an EQC, or more than 0.8V.

[0039] An ozone aqueous solution contacts ozone gas in the acid aqueous solution adjusted to five or less pH, and is prepared. The thing which was made to generate using a solid electrolyte electrolytic decomposition process ozonator and which carry out an ozone gas activity is desirable. Although the ozone gas generated with the silent discharge method by using air or oxygen gas as a raw material is used by the conventional method, the ozone gas concentration obtained by this method is about number vol% at the maximum. According to the solid electrolyte electrolytic decomposition process, the ozone gas of about [ 20vol% ] concentration can be generated at the maximum, and the ozone aqueous solution in which the high-concentration, i.e., are high, oxidation engine performance is shown can be manufactured.

[0040] As for the acid aqueous solution in which ozone gas is contacted, it is desirable to be adjusted to five or less with acids, such as a nitric acid. pH of an ozone aqueous solution and the relation of the amount of dissolution of an oxide film are shown in drawing 3 . The unit of the amount of dissolution is the ratio of the amount of dissolution by the ozone aqueous solution at the time of setting the amount of dissolution by the permanganic acid method to 1, and the amount of dissolution by the ozone aqueous solution to the amount [ in other words ] of dissolution by the permanganic acid method. Temperature of an ozone aqueous solution was made into 50 degrees C. The amount of dissolution of an oxide film rose rapidly by five or less pH, and showed the soluble ability more than a permanganic acid method and an EQC. Moreover, the oxidation-reduction potential of a with a pH of five or less ozone aqueous solution was higher than 1000mV.

[0041] Chromium exists with the chemical form of  $\text{Cr}_2\text{O}_7^{2-}$  which  $\text{HCrO}_4^-$ ,  $\text{CrO}_4^{2-}$ , or this condensed. Therefore, Cr  $\text{O}_3$  oxidizes with an ozone aqueous solution, and it is thought that it becomes easy to dissolve at a reaction like a bottom type.

[0042]  $\text{Cr}_2\text{O}_3 + 3\text{O}_3 + 2\text{H}_2\text{O} \rightarrow 2\text{CrO}_4^{2-} + 4\text{H}^+ + 3\text{O}_2$   $\text{Cr}_2\text{O}_3 + 3\text{O}_3 + \text{H}_2\text{O} \rightarrow \text{Cr}_2\text{O}_7^{2-} + 2\text{H}^+ + 3\text{O}_2$  aqueous solution goes up so that aqueous solution temperature is low, but oxidation reaction of a chromic-acid ghost is promoted, so that temperature is high. Therefore, it is thought that suitable temperature conditions to dissolve an oxide film with which the dissolution concentration of ozone and the facilitatory effect of oxidation reaction balance exist.

[0043] As for the temperature of the ozone aqueous solution used as an oxidizer, it is desirable that it is the range of 50-100 degrees C. The relation of the ozone level and solution temperature in the ozone aqueous solution of pH3, pH4, and pH5 and the relation between the amount of dissolution of an oxide film (O, \*, and < show) and solution temperature are shown in drawing 4 . The unit of the amount of dissolution is the ratio of the amount of dissolution by the ozone aqueous solution at the time of setting the amount of dissolution by the permanganic acid method to 1, and the amount of dissolution by the ozone aqueous solution to the amount [ in other words ] of dissolution by the permanganic acid method. It is not concerned with the value of pH of an ozone aqueous solution, but the ozone level is high, so that solution temperature is low.

[0044] On the other hand, the amount of dissolution of the oxide film in the ozone aqueous solution of pH3 and pH4 is low [ the 40 degrees-C and elevated-temperature side by the side of low temperature ] at 95 degrees C. Although an ozone level is high with a low-temperature solution as for this, since solution temperature is low, oxidation reaction does not progress, but with an elevated-temperature solution, although oxidation reaction is promoted, since the ozone level is low, it is shown that oxidation was not fully performed.

[0045] As mentioned above, in the ozone aqueous solution of pH3 and pH4, it was checked that a thing with the high (the dissolution property more than a permanganic acid method and an EQC is shown) dissolution property of an oxide film is shown by the 50-80-degree C temperature requirement, and an oxide film can be dissolved at a low temperature as compared with a conventional method.

[0046] A oxidation-reduction potential is mentioned for a permanganic acid solution, a potassium



permanganate solution, etc. as a solution of a certain drugs an ozone aqueous solution, an EQC, or more than 0.8V. If about 100 ppm or more the permanganic acid solution or potassium permanganate solution 10000 ppm or less of a density range is used, a oxidation-reduction potential will be set to 800mV or more, and the good oxidation engine performance will be obtained.

[0047] As a reducing agent used in the reduction dissolution processes 22 and 24, a dicarboxylic acid aqueous solution is used preferably. An oxalic acid aqueous solution is used especially preferably. As for the concentration of an oxalic acid aqueous solution, it is desirable that it is the range of about 1000 ppm - 50000 ppm.

[0048] The relation of the concentration of an oxalic acid aqueous solution and the rate of dissolution of a chromium nickel ferrite in the solution temperature of 95 degrees C is shown in drawing 5. Although the rate of dissolution increases along with concentration lifting by the oxalic acid concentration of 1000 ppm or more, when maximum is reached and concentration becomes high from this near the oxalic acid concentration of 30000 ppm, it shows a downward tendency to reverse.

[0049] The oxide solvent power of oxalic acid increases in proportion to concentration. However, pH of an oxalic acid aqueous solution is 30000ppmm, as a result of the formation constant of an oxalic acid complex becoming small and it becoming impossible to hold in a solution as an oxalic acid complex, in order to fall by lifting of acid concentration. It is thought that the maximum of the amount of dissolution exists near.

[0050] As for the temperature of a dicarboxylic acid aqueous solution, it is desirable to hold in the range of 50 to 100 degrees C. The relation between the temperature of the dicarboxylic acid aqueous solution at the time of reduction dissolution and the rate of dissolution of an oxide film (hematite) is shown in drawing 6. Here, hematite is 1 g/L and oxalic acid is 2 g/L.

[0051] The reduction reaction of the ferric acid ghost in the inside of an aqueous solution is promoted, so that temperature is high, so that clearly from drawing. Therefore, when it thinks by the reduction dissolution independent, when it takes not boiling an aqueous solution into consideration, 95-degree-C order is desirable [ it is so advantageous that the temperature of a dicarboxylic acid aqueous solution is high, and ].

[0052] When performing system decontamination processing especially, it is desirable to make an oxidation process and a reduction process into the same temperature conditions. It can process continuously, without performing the temperature up of the decontamination liquid between processes, or a temperature fall, and compaction of working hours is possible.

[0053] According to this example, by the oxidation / reduction decontaminating method which combined oxidizing melting and reduction dissolution efficiently, the oxide film which exists between the radioactive substance of metal structure material, such as piping of a reprocessing facility and its related facility, a device, and a structural part, itself and the radioactive substance, and a metal base material is dissolved, and high decontamination of the clearance engine performance can be performed.

[0054] By repeating oxidation / reduction decontamination, the elimination factor of the oxide film on the front face of a base material can be raised further.

[0055] The strong oxidizing power of ozone can be effectively used by using as an oxidizer the ozone aqueous solution adjusted by dissolving the ozone which is an oxidizing quality gas in the aqueous solution of suitable water quality conditions. Moreover, the secondary trash yield resulting from a decontamination reagent can be reduced.

[0056] Since the oxidizing melting engine performance by ozone is high, even if the temperature of the aqueous solution at the time of decontamination is comparatively low, sufficient decontamination force is acquired. Therefore, from the conventional chemistry decontamination method, it can carry out at low temperature and energy and working hours required for temperature up can be reduced.

[0057] A oxidation-reduction potential's being equivalent to an ozone aqueous solution or the oxidation decontamination effect of having excelled when using the solutions (a permanganic acid solution, potassium permanganate solution, etc.) of a certain drugs as an oxidizer more than 0.8V can be acquired. Moreover, if it is made to react with drugs, such as oxalic acid, in case waste fluid is disposed of, it becomes water and a carbon dioxide, and since trash serves as only some metal ions, the secondary trash



yield resulting from a decontamination reagent can be reduced.

[0058] Since the reduction decontamination effect can disassemble decontamination waste fluid into water and a carbon dioxide highly by using dicarboxylic acid, such as oxalic acid, as a reducing agent, the secondary trash yield resulting from a decontamination reagent can be reduced.

[0059] (Example 2) The decontamination method concerning this example carries out direct water flow supply of the decontamination reagent to a reprocessing facility system using a decontamination reagent supply circulation system, and performs decontamination processing.

[0060] As shown in drawing 7, a decontamination reagent supply circulation system consists of a line which connects the decontamination reagent tank 8, the ozone generator 6, the infusion-of-drug tank 7, the circulation feed pump 9, the heating heater 10, the decontamination reagent purification system 11, the decontamination reagent decomposition system 12, and these.

[0061] Although the equipment of a simple substance is sufficient as the reprocessing facility 5 which is an object for decontamination, system piping including two or more reprocessing facilities is sufficient as it. By establishing the entry and outlet of a decontamination reagent in these systems, and connecting a line, a decontamination reagent supply circulation system is connected and a decontamination reagent endless loop is constructed.

[0062] As an oxidizer, the solutions (a permanganic acid solution, potassium permanganate solution, etc.) of a certain drugs can be used that an ozone aqueous solution and a oxidation-reduction potential are equivalent to an ozone aqueous solution, or more than 0.8 V, for example.

[0063] As a reducing agent, dicarboxylic acid aqueous solutions, such as oxalic acid, can be used.

[0064] As an ozonator 6, it is desirable to use a solid electrolyte electrolytic decomposition process ozonator. A black light, ozone irradiation equipment, etc. can be used as a decontamination reagent decomposition system 12.

[0065] First, before decontaminating, a nitric acid (3-8M) is incorporated from a reprocessing facility, all the systems that contain the section for decontamination in 95 degrees C after temperature up are circulated, and a system is washed. Clearance dissolution of the matter which dissolves in a nitric acid is carried out beforehand by this, and the burden to decontamination liquid is reduced as much as possible.

[0066] Temperature up of the water is carried out to all the systems containing the section for decontamination to about 50 degrees C - 100 degrees C at a beam and the heating heater 10 after washing.

[0067] After temperature up, in oxidation decontamination, an ozone aqueous solution is produced by generating ozone gas with an ozonator 6 and dissolving underwater, and it pours into it to the decontamination tank 8, and it adjusts to it so that it may become concentration predetermined in a system. At this time, it is desirable to add acids, such as a nitric acid, in the water before ozone dissolution, and to adjust pH of an ozone aqueous solution to five or less. Although saturated concentration changes with temperature, as for ozone aqueous solution concentration, it is desirable to be referred to as about 3-30 ppm in the degree of about 50 degrees C - 100 degree C.

[0068] The ozone aqueous solution adjusted to concentration predetermined by the decontamination tank 8 is sent out to a decontamination system line by the circulation feed pump 9.

[0069] Moreover, as an oxidizer, in using a permanganic acid solution or a potassium permanganate solution, it pours in to the decontamination tank 8 using the infusion-of-drug tank 7, so that it may become predetermined concentration (100 ppm - 10000 ppm).

[0070] Oxidation decontamination is carried out standardly for about 2 to 5 hours. The oxidizer after oxidation decontamination termination has pollutants, such as the radioactive substance, removed after decomposition and in the decontamination reagent purification system 11 by the decontamination reagent decomposition system 12, and serves as nitric-acid water or water. A reducing agent is added in this water and it moves to a reduction step.

[0071] At the time of reduction decontamination, from the infusion-of-drug tank 7, oxalic acid is added to the decontamination tank 8 so that it may become predetermined concentration (1000 ppm - 30000 ppm). It sends out to a decontamination system line by the circulation feed pump 9, dissolving and stirring oxalic acid by the decontamination tank 8.

[0072] Reduction decontamination is standardly carried out at 95 degrees C for about 5 hours. After the reducing agent after reduction decontamination termination has pollutants, such as the radioactive substance, removed in the decontamination reagent purification system 11, it is disassembled by the decontamination reagent decomposition system 12. In repeating oxidation / reduction process, ozone gas is contacted to the water obtained by disassembling a reducing agent, or permanganic acid or potassium permanganate is added, an oxidizer is prepared, and it shifts to oxidation decontamination.

[0073] Such a step is repeated if needed. Although the count of a repeat is based also on the thickness and the gestalt of an oxide skin, its about 2 times are usually desirable. Moreover, in this example, although it shifted to reduction decontamination after performing oxidation decontamination, sequence may be made into reverse and reduction decontamination may be performed first.

[0074] Decontamination processing can be carried out efficiently, without using a special decontamination tub and a decomposition tub by such configuration, about the system part which can construct an endless loop, when decontaminating the whole system or a part.

[0075] Moreover, dicarboxylic acid is disassembled into water and carbon dioxide gas by UV irradiation, ozone exposure, etc., and an ozone aqueous solution is returning to the system of a reprocessing facility as a nitric-acid solution after ozone clearance, and can reduce substantially generating of the secondary trash resulting from a decontamination reagent.

[0076] (Example 3) The decontamination method concerning this example holds an oxidizer and a reducing agent in the decontamination tub of respectively dedication, is immersed in these decontamination tubs in metal structure material, and performs decontamination processing.

[0077] As shown in drawing 8, the heater 18 is formed in each of the front washing tub 14, the oxidation tub 15, the reduction tub 16, and the last washing tub 17.

[0078] The nitric acid (about 3M- about 8 M) is held in the front washing tub 14 and the last washing tub 17, and it is maintained at about 50 degrees C - about 100 degrees C of solution temperature by the heater 18.

[0079] The 3 ppm - 30 ppm ozone aqueous solution is held in the oxidation tub 15 as an oxidizer, and it is maintained at 50 degrees C - 100 degrees C of solution temperature by the heater 18. Instead of an ozone aqueous solution, a oxidation-reduction potential may use as an oxidizer the solutions (for example, a 100 ppm - 10000 ppm permanganic acid solution or a potassium permanganate solution etc.) which are this ozone aqueous solution, an EQC, or more than 0.8V.

[0080] The 1000 ppm - 30000 ppm oxalic acid aqueous solution is held in the reduction tub 16 as a reducing agent, and it is maintained at 50 degrees C - 100 degrees C of solution temperature by the heater 18. Other dicarboxylic acid aqueous solutions may be used instead of an oxalic acid aqueous solution as a reducing agent.

[0081] As a decontamination object 13, steady equipment, a components simple substance, or metal refuse in a decontamination pin center, large etc. is desirable.

[0082] Such a decontamination object 13 is first immersed in the nitric-acid solution in the front washing tub 14 for about 2 hours. Since the radioactive substance of fusibility is dissolved and removed by the nitric acid with the nitric acid in the front washing tub 14, it can reduce the burden to a decontamination reagent to it. The nitric acid used for front washing is transported to the high speed circuit or nitric-acid processing system of a reprocessing facility as it is.

[0083] The decontamination object 13 washed the front is immersed in the ozone aqueous solution in ejection and the oxidation tub 15 from the front washing tub 14 for about 2 to 5 hours, and oxidation decontamination is performed. Subsequently, the decontamination object 13 is immersed in the oxalic acid aqueous solution in ejection and the reduction tub 16 from the oxidation tub 15 for about 5 hours, and reduction decontamination is performed.

[0084] If needed, the immersion to the oxidation tub 15 and the reduction tub 16 is repeated, oxidation / reduction repeat decontamination of the decontamination object 13 is performed, and the oxide film which exists between the radioactive substance and the radioactive substance, and a metal base material is dissolved. Usually, it is desirable to repeat oxidation / reduction process twice.

[0085] In the meantime, a decontamination reagent is supplied in a decontamination tub if needed, and

the decontamination engine performance is maintained by maintaining a decontamination reagent at a predetermined density range.

[0086] For example, the ozone aqueous solution concentration in the oxidation tub 15 falls by the autolysis of ozone, or consumption by oxidation reaction. As shown in drawing 9, it depends for the oxidation-reduction potential of an ozone aqueous solution on an ozone level. Therefore, lowering (namely, oxidation performance degradation) of an ozone level can be supervised on real time by measuring the oxidation-reduction potential of an ozone aqueous solution continuously. The oxidizing power of an ozone aqueous solution is controlled by adjusting the ozone amount of supply based on the obtained measured value, and adjusting an ozone level to a suitable range, and effective decontamination processing can be performed. <BR> [0087] Although the monitor of the concentration lowering by such oxidation-reduction potential measurement is also possible when using a permanganic acid solution or a potassium permanganate solution as an oxidizer, concentration lowering may be supervised by measuring conductivity.

[0088] Finally, it is immersed in the nitric-acid solution of the last washing tub 17 for about 30 minutes, the decontamination object 13 taken out from the reduction tub 16 is washed, and resoiling is prevented.

[0089] According to this example, continuous duty can be used, or reproduced and carried out several times, without using a decontamination reagent as waste fluid by activity once.

[0090] Moreover, efficient decontamination processing can be performed by supervising and adjusting the engine performance of a decontamination reagent on real time.

[0091] (Example 4) The decontamination method concerning this example has the same configuration as the decontamination method of an example 3, and a basic target except using ultrasonic cleaning together during washing or after washing and during decontamination, or after decontamination.

[0092] As shown in drawing 10, the ultrasonic vibrator 19 is built in the washing-before this example tub 14, the oxidation tub 15, the reduction tub 16, and the last washing tub 17.

[0093] An ultrasonic vibrator 19 can bear an about 100-degree C elevated temperature. An ultrasonic frequency is suitably chosen by about 20kHz - about 100kHz.

[0094] On the occasion of ultrasonic cleaning, it is not necessary to necessarily carry out continuous running of the ultrasonic vibrator 19. In order to prevent that vibrator 19 generates heat and a life becomes short, dispatch and a halt may be repeated by turns.

[0095] The comparison of an oxide film elimination factor with the decontamination processing which is not used together with the decontamination processing which used ultrasonic cleaning together to drawing 11 is shown. It decontaminated on the same conditions as an example 3 except using ultrasonic cleaning together. At the time of each tub immersion, ultrasonic cleaning operated the ultrasonic vibrator 19 at the interval of the dispatch for 20 minutes, and a halt with the frequency of about 28kHz, and performed it.

[0096] The elimination factor after the 1st decontamination cycle (1st) is improving from 68% to 89% according to concomitant use of ultrasonic cleaning so that clearly from drawing 11. Moreover, the final coat elimination factor is also improving.

[0097] According to this example, on a base material front face, the radioactive substance, an oxide film, etc. which were dissolved by oxidation / reduction decontamination can remove by a residual or performing ultrasonic cleaning, even if it is carrying out the reattachment. Therefore, the rate that a new field contacts a decontamination reagent also increases, and improvement in the clearance engine performance and compaction of decontamination time amount are possible.

[0098]

[Effect of the Invention] As stated above, according to this invention, by the oxidation / reduction decontaminating method which combined oxidizing melting and reduction dissolution efficiently, the oxide film which exists between the radioactive substance of metal structure material, such as piping of a reprocessing facility and its related facility, a device, and a structural part, and the radioactive substance, and a metal base material is dissolved, and high decontamination of the clearance engine performance can be performed. Moreover, the yield of the secondary trash resulting from a decontamination reagent can be reduced.